Environmentally friendly lubricants through a zero waste process

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ABSTRACT

Tri-esters of fatty acids with polyols can be easily prepared through direct esterification of different acids with the polyol in the presence of amorphous solid acid catalysts. Conversion close to 100% and very high selectivity to triesters can be obtained in the presence of a silica zirconia amorphous catalyst. Activity and selectivity can be due to the presence of very well dispersed Lewis acid sites consisting in tetrahedrally coordinated Zr ions that are resistant to water formed during reaction as shown by FT IR spectroscopy.

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1. Introduction

World demand for lubricants and hydraulic fluids is over 40 million tonnes. Among these, the use of bio-lubricants in Europe is estimated to be around 130.000 tonnes and foreseen to reach 420.000 tonnes within 2020 [1]. Such a high increase in the substitution of traditional lubricants with biodegradable and renewable ones mainly derives from environmental concerns and awareness, considering that about 50% of hydraulic liquids end up into the environment due to total loss applications, spillage, evaporation and accidents, thus resulting in severe pollution of soil, water and air [2,3]. Beside this consumers are even more prone to use products from renewable raw materials instead of traditional ones, thus influencing the market of bio-products which is supposed to reach 700 billion dollars by 2018, and in turn the research and development of new products [4].

Vegetable oil based lubricants offer several advantages with respect to mineral oil based ones: they come from renewables, they show higher lubricant properties with respect to mineral oils, high viscosity and high viscosity index, higher flash point that makes them advantageous as far as the risk of accident is concerned. They are environmentally friendly as they are easily degraded in the environment whereas 1 l mineral oil can pollute 1 million liters drinking water. Moreover, they do not contain polycyclic aromatic hydrocarbons (PHA) [5] the most measured and studied toxic agents for workers exposed to metal cutting fluids. These features result in important benefits from both the environmental point of view and the safety of workers involved in the use of industrial lubricants [6].

On the other hand, biolubricants based on vegetable oils suffer from poor oxidative and thermal stability. The latter strongly depends on the presence of an hydrogen atom in β position with respect to the ester groups of triglycerides (Scheme 1), whose tendency to the β-elimination reaction leads to an easy molecular degradation [7].

For this reason more hindered esters derived from the esterification of free fatty acids (FFAs) with polyols such as trimethylolpropane (TMP) or pentaerythritol (Scheme 2), are shown to be more stable from the thermal point of view, due to the absence of hydrogen atoms in beta position. In spite of the use of a polyol other than glycerol, that is "non-natural", this kind of lubricants contains up to 90% of carbon derived from biomass, thus, deserving the European EcoLabel or the one of USDA Biopreferred product.

On the other hand, these tri-esters, although, transesterification of fatty acid methylesters with the polyol in the presence of sodium methoxide or alkalyne hydroxides can be used [8,9] and a kinetic model for this reaction has been proposed [10], are usually prepared by fatty acids esterification catalysed by homogeneous systems, namely H_2SO_4, HCl, perchloric or *p*-toluensulphonic acid

Scheme 1. Degradation of triglycerides via β-elimination reaction.

[11,12] thus, entailing corrosion problems and production of significant amounts of inorganic salts and waste water due to the need of neutralization and washing steps. Heterogeneous SnO is a valuable alternative, showing high activity at $T > 160\,°C$, but it forms small amounts of soaps that have to be split for a deep metal trace removal, thus requiring another acidic treatment and several washing steps. In spite of the beneficial effects drawn by the use of heterogeneous catalysts, only few papers deal with the use of solid acids for this purpose [13,14]. Here we wish to report on the use of amorphous mixed oxides as effective solid catalysts for the production of polyol-esters to be used as high quality bio-lubricants.

2. Experimentals

2.1. Materials and methods

$SiO_2–Al_2O_3$ (SA = 485 m^2/g, PV = 0.79 mL/g) was purchased from Sigma–Aldrich. $SiO_2–TiO_2$ (SA = 340 m^2/g, PV = 1.2 mL/g), $SiO_2–ZrO_2$ 3 (3.0% ZrO_2, SA = 455 m^2/g, PV = 0.71 mL/g) and $SiO_2–ZrO_2$ 5 (4.7% ZrO_2, SA = 304 m^2/g, PV = 1.62 mL/g) were kindly supplied by Grace Davison, Columbia, USA.

Technical grade oleic acid (C18), caprilic acid (C8-C10) and TMP, purchased from Merck Millipore were used for the experiments, whereas, pelargonic acid (C9)(96%), neopentylglicol (99%) and pentaerythritol (98%) were purchased from Sigma–Aldrich.

2.2. Catalytic tests

In a typical catalytic run the catalyst was used without any pretreatment and loaded on a three necked glass reactor with oleic acid (35 g, 124 mmol) and TMP (5.2 g). When the reaction was carried out with an excess polyol 6.1 g of TMP were used. The reactor was also equipped with a Claisen condenser, a thermometer and a gas bubbler in order to flush the reactor by a weak N_2 flow (0.2 mL/min). The reaction was monitored by acid–base titration with NaOH (0.1 N) and phenolphtalein by dissolving the oil in a mixture of 1:2 EtOH/diethylether according to the NGDC10–1976 method. The ester distribution was determined by GC analysis (Agilent 7890N equipped with an on column injector, an AT-1 column, 12 m × 0.32 mm × 0.1 μm). Before injection the fatty mixture was derivatized by using N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) together with a standard mixture comprising

C19:0 methylester, mono-, di-, and triglyceride according to the UNI22053 procedure.

For the recycling tests the catalyst was separated from the product by simple centrifugation or filtration, washed with acetone and used again without any further pre-treatment for the following test.

DR-UV–vis spectra were collected, from 190 to 600 nm, on pure samples using a Praying—Mantis Diffuse Reflectance Accessory (Harrick Sci, USA) mounted in a Evolution 600 spectrophotometer (Thermo). A Spectralon® disk was used as reference material for background measurement. All the samples were measured under ambient conditions.

The FT-IR studies of pyridine adsorption and desorption were carried out with a FTS-60 spectrophotometer equipped with mid-IR MCT detector purchased from BioRad. The experiments were performed on a sample disk (15–20 mg) after a simple calcination treatment (180 °C, 20 min air + 20 min under vacuum). One spectrum was collected before probe molecule adsorption as a blank experiment. Therefore, pyridine adsorption was carried out at room temperature, and the following desorption steps were performed from room temperature to 250 °C. The spectrum of each desorption step was acquired every 50 °C after cooling the sample. For water saturated-$SiO_2–ZrO_2$ sample, treatment with saturated H_2O vapour at room temperature was carried out prior to the same procedure of Py adsorption above described. For quantitative analysis the amount of adsorbed pyridine ($mmol_{Py}/g_{cat}$) was calculated on the basis of the relationship reported by Emeis [15] from the integration of the band around 1450 cm^{-1}.

Biodegradability was evaluated through the modified Sturm test OECD 301 B (CO_2 evolution test).

3. Results and discussion

The use of amorphous mixed oxides such as $SiO_2–Al_2O_3$, $SiO_2–TiO_2$ and $SiO_2–ZrO_2$ as solid acid catalysts has already been reported due to their interesting performances in the esterification of highly acidic oils with methanol for the production of biodiesel [16]. One of the main advantages observed with these materials was their high resistance to the water formed during reaction. Thus, not only they were found to be able to lower the acidity of several oils with a free fatty acid (FFA) content up to 15% down to <0.5% in 1 h, but they also showed excellent activity even with fatty acid mixture with up to 98% free fatty acids, as in the case of tall oil fatty acids, a by product of the Pulp & Paper industry. The acidity of this oil could be lowered from 98% to 8.5% in 1 h at 180 °C by using a methanol to oil molar ratio of 10:1.

The same oxides were therefore, tested in the esterification of FFAs with trimethylolpropane (TMP) in order to obtain the corresponding triesters (Table 1).

Among the four acidic solid tested, namely $SiO_2–Al_2O_3$, $SiO_2–TiO_2$ and two different $SiO_2–ZrO_2$, the latter with an higher content of ZrO_2 resulted to be the most performing one, leading to
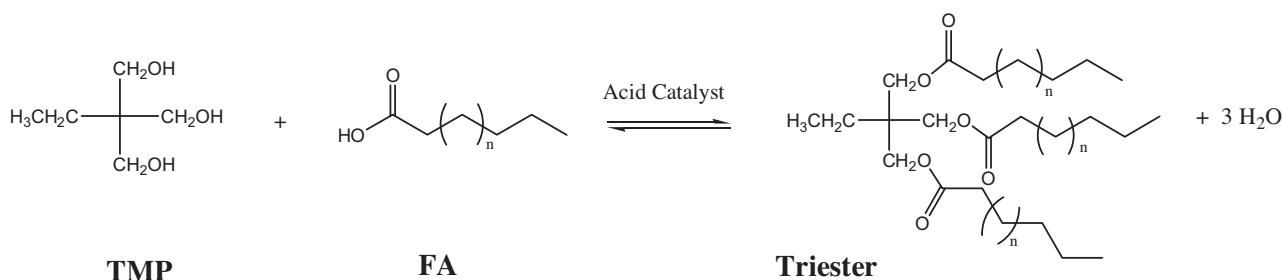
Scheme 2. Formation of tri-ester from trimethylolpropane and fatty acids.

Table 1
Esterification of different fatty acids with TMP and other alcohols by using solid acid catalysts (200 °C, 6 h, 5% excess of fatty acid).

Entry	Fatty acid	Catalyst	Polyol	Catalyst% wt	Conv %
1	Oleic (C18)	SnO	TMP	10	92.6
2		SiO_2-Al_2O_3	TMP	10	85.9
3		SiO_2-TiO_2	TMP	10	96.8
4		SiO_2-ZrO_2 3	TMP	10	90.2
5		SiO_2-ZrO_2 5	TMP	10	99.8
6		SiO_2-ZrO_2 5	TMP	5	99.3
7		SiO_2-ZrO_2 5	TMP	2.5	99.0
8[a]		SiO_2-ZrO_2 5	TMP	2.5	97.0
9[a]		SiO_2-ZrO_2 5	Pentaerythrol	2.5	99.0
10[a]		SiO_2-ZrO_2 5	NPG	2.5	92.0
11[a]	Caprilic (C8–C10)	SiO_2-ZrO_2 5	TMP	2.5	95.0
12[a]		SiO_2-Al_2O_3	TMP	2.5	92.0
13[a]		SiO_2-TiO_2	TMP	2.5	92.0
14[a]	Pelargonic (C9)	SiO_2-ZrO_2 5	TMP	2.5	>98.0
15[a]		SiO_2-Al_2O_3	TMP	2.5	94.0
16[a]		SiO_2-TiO_2	TMP	2.5	94.0

[a] Reaction carried out with 5% excess of polyol.

99.8% conversion when working with a slight excess of acid in the starting mixture (entry 5).

The process resulted to be efficient also by using polyols other than TMP, such as pentaerythrol and neopentyl glycol (entries 9 and 10). In particular with pentaerythrol 99% conversion can be reached.

It is also worth mentioning that no significant differences in activity were found going from long chain oleic acid to short chain C8 and C9 fatty acids (entries 11–16). This is quite unusual as oleic acid was found to react much slower than caprilic in the presence of both supported sulfuric acid and sulfonic resin, whereas, the opposite behavior was found in the presence of a supported enzyme [14]. Also in the synthesis of monoglycerides over acidic zeolites or 3-mercaptopropyl (methyl) dimethoxysilane (MPMDS) modified MCM41 oleic acid was always found to be much less reactive than lauric acid (C12) [17].

Different parameters have been taken into account in order to optimize the process, in particular the catalyst loading and the alcohol/acid molar ratio.

The amount of catalyst can be lowered without affecting conversion in a significant way (entries 6 and 7). On the other hand, although an excess of FFAs gave a higher conversion, issues linked with the separation of the product from exceeding fatty acids prompted us to carry out the reaction with an excess of polyol, anyway observing 97% of conversion (entry 8).

As far as the catalyst role is concerned, a striking difference between the two silica zirconia materials was observed. Fig. 1 shows the esters distribution obtained in the presence of the two silica zirconia compared with the one obtained with SnO. It is apparent that although with SnO very good results are obtained, it is only over SiO_2–ZrO_2 5 that a yield higher than 95% can be obtained due to both high conversion and very high selectivity. Thus, it should be noted that di-esters are totally absent in the final mixture.

The very high selectivity translates into excellent physical properties of the raw triesters. In fact viscosity and viscosity index are affected by the presence of uncontrolled concentrations of partial esters: the higher the concentration of —OH groups, the higher the viscosity [16].

Table 2 sums up the features of the esters just after separation from the catalyst by centrifugation, all the parameters are close to those reported in the literature [18]. In order to shed some light on the features affecting activity and selectivity in this reaction, we carried out a spectroscopic study of the different catalysts. FT-IR spectra of adsorbed pyridine are known to show many peaks ranging from 1400 to 1700 cm^{-1}. Pyridine bound to Lewis acid sites
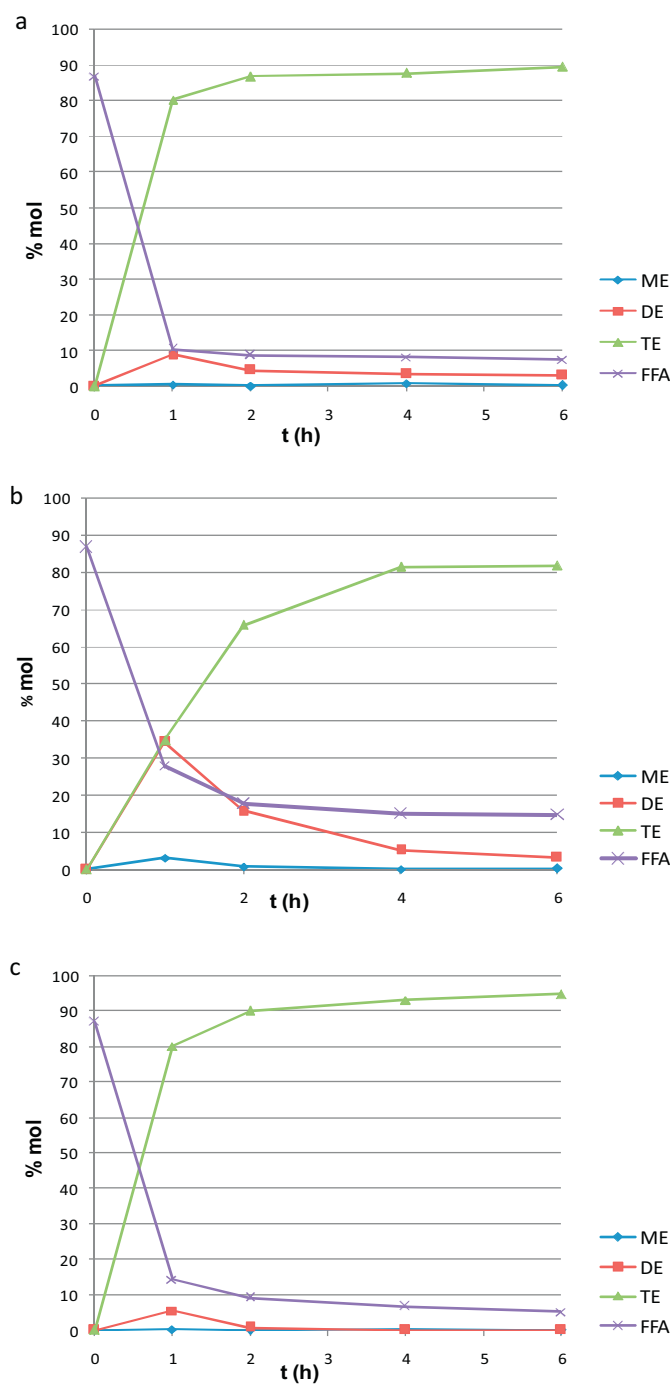
Fig. 1. Product distribution in the esterification of oleic acid with trimethylolpropane (a) with SnO; (b) with SiO_2–ZrO_2 3; (c) with SiO_2–ZrO_2 5. (ME = monoesters; DE = diesters; TE = triesters; FFA = Free fatty acids).

(L) is usually assigned to a first band around 1450 cm^{-1} and a second one around 1610 cm^{-1}, whereas, an absorption at 1550 cm^{-1} followed by a peak near 1640 cm^{-1} is related to the presence of Brønsted acid sites (B). Analysis of the spectra shows that only on the surface of SiO_2–Al_2O_3 Brønsted acid sites are present, whereas, on both silica titania and silica zirconia only Lewis acid sites can be detected (Table 3). The different distribution of acidity in Zr and Al systems has already been highlighted for other esterification reactions [19,20]. The high activity and selectivity of the SiO_2–ZrO_2 5 catalyst may be ascribed to the presence of Lewis acid sites.
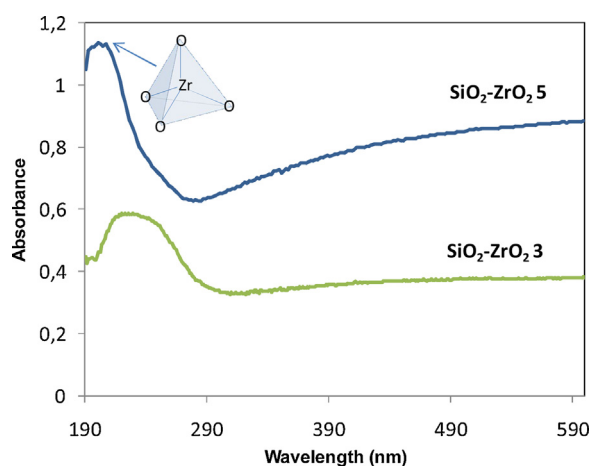
Table 2
Viscosity, viscosity index and pour point (PP) measured for the triesters prepared with solid catalysts.

Fatty acid	Sample	Viscosity 40 °C(cSt)	Viscosity 100 °C(cSt)	Viscosity index	PP	(°C)
C18	SiO$_2$-TiO$_2$	46.7	9.1	181		−25
	SiO$_2$-ZrO$_2$ 5	46.5	9.3	188		−27
C8–C10	SiO$_2$-ZrO$_2$ 5	19.9	4.3	124		−60
C9	SiO$_2$-ZrO$_2$ 5	22.3	4.5	118		−54

Table 3
Features of the mixed oxides in terms of pore diameter (PD), surface area (BET), Pore volume (PV) and density of acidic sites.
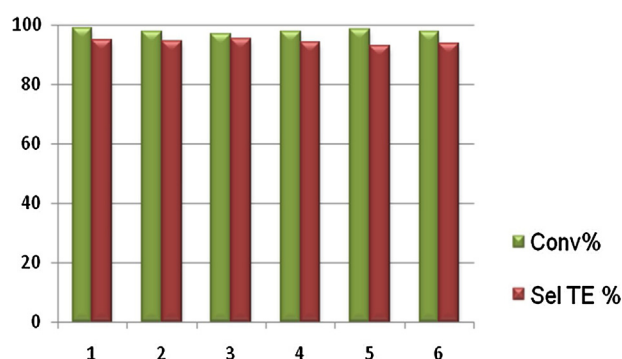
Catalyst	PD (nm)	BET (m^2/g)	PV (ml/g)	BET/PV(m^2/mL)	Acidity	(mmol$_{py}$ /g)
					L	B
SiO$_2$−Al$_2$O$_3$	3.3	485	0.79	614	0.163	0.039
SiO$_2$−TiO$_2$	8.4	297	1.26	236	0.014	–
SiO$_2$−ZrO$_2$ 5	10.6	304	1.62	187	0.033	–

Fig. 2. DRUV spectra of SiO$_2$−ZrO$_2$ 3 and SiO$_2$−ZrO$_2$ 5.

Fig. 3. Recycling tests of esterification of oleic acid with trimethylolpropane with SiO$_2$−ZrO$_2$ 5.

It is well known that pure ZrO$_2$ is weakly acidic and to improve its acid properties strategies including sulfonation and mixing with other oxides have been envisaged. However, one of the main drawbacks of Zr based catalysts is their low surface area making the Zr site not easily accessible to reactants thus promoting intensive efforts to improve this parameter by using meso-structured silica with very high surface area, open porous structure and narrow pore size distribution as supports [21]. In particular SBA 15 silica supports with a tunable large sized pore structure and high hydrothermal stability has been often used as the support for zirconocene exchanged materials able to promote both the transesterification of raw vegetable oil and the esterification of fatty acids with methanol to produce Biodiesel at 200 °C and with a MeOH to oil molar ratio 30:1 [22–24].

The amorphous silica zirconia material we are using in the present paper shows pore size comparable to the Zr SBA catalyst (namely 10.6 vs 10.4 nm) [22] but a higher PV (1.62 vs 1.38 mL/g) and a lower surface area (304 vs 772 m^2/g). It is interesting to note that an empiric relationship between BET, PV and acidic activity, the lower the ratio BET/PV the higher the activity, was already observed by Jacobs et al. [25] and Shanks et al. [26] for the esterification of fatty acids with glycerol or methanol over sulfonic modified mesoporous silicas. According to this hypothesis silica titania, with a BET/PV ratio similar to the one of silica zirconia, shows a slightly lower activity due to the lower number of acidic sites.

In order to better elucidate the dispersion degree of Zr ions and its coordination, diffuse reflectance UV spectroscopy has been performed. From the spectra the sharp difference between the two catalysts is evident (Fig. 2). Thus the 5% catalyst shows an intense adsorption band at 195–200 nm, that is ascribed to ligand-to metal charge transfer from an O$^{2−}$ to an isolated Zr^{4+} ion in a tetrahedral configuration [27]. On the other hand the SiO$_2$−ZrO$_2$ 3 system, that revealed to be much less active (Fig. 1b), shows a broad adsorption band centred at 230 nm. The shift to lower energy is diagnostic of the presence of ZrO$_2$ of mixed tetragonal and monoclinic phase [28].

As far as the stability of the SiO$_2$−ZrO$_2$ 5 catalyst is concerned, up to six catalytic runs were performed without observing any significant decrease in activity nor in selectivity to tri-ester (Fig. 3). This is very important considering that any demanding pre-treatment or calcination step is necessary between one catalytic run and the following one, but a simple separation and washing of the solid acid. On the contrary the activity of Zr SBA 15 in the transesterification of palm oil with methanol gradually decreased after the fourth run and could only be restored by calcinating the catalyst at 550 °C for 5 h [22].

The great potential of the proposed catalyst, namely SiO$_2$−ZrO$_2$ 5, is mainly based on its peculiar resistance to water formed during the esterification reaction. One of the weakest points of Lewis acids is linked to their sensitivity to water. In order to highlight this feature, IR analysis of adsorbed pyridine were carried out on the bare catalyst and on the catalyst exposed to a prior saturation with water, according to a technique recently suggested by Hara [29–31].

From the spectra reported (Fig. 4) it is evident that even after saturation of the catalyst surface with water, signals ascribable to Py interacting with Lewis acid sites (1450 cm^{-1} and 1610 cm^{-1}) are still visible.

In particular the total amount of Lewis acid sites on dehydrated SiO$_2$−ZrO$_2$ and on water saturated-SiO$_2$−ZrO$_2$ after degassing at 150 °C resulted to be 0.033 mmol$_{Py}$/g$_{cat}$ and 0.019 mmol$_{Py}$/g$_{cat}$
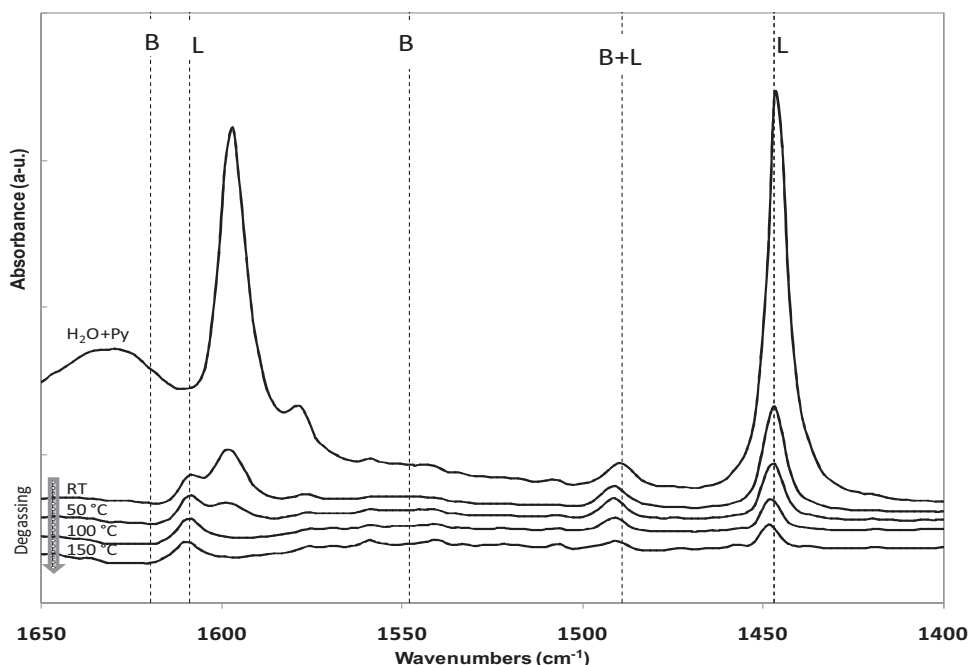
Fig. 4. IR spectra of adsorbed pyridine on water-saturated SiO_2–ZrO_2.

respectively. This clearly shows that a significant amount of unsaturated Zr ions still act as Lewis acid sites even in the presence of water, thus showing their high tolerance to the reaction conditions.

The remarkable resistance of this material to water poisoning can then be due to the presence of ZrO_4 tetrahedra that are not decomposed by water, but interact with water and can be easily exchanged by nucleophilic reactant.

Moreover, no leaching of zirconium was observed upon ICP analysis of the product.

The true heterogeneous nature of the catalyst is crucial in making the process more sustainable with respect to existing systems, due to significant reduction of inorganic wastes and washing steps.

The absence of metallic soaps, one of the main drawbacks of tin catalysed reactions, allows one to avoid purification steps, thus making this procedure more sustainable. On the other hand low amount of partial esters allows the product to perform very well.

4. Conclusions

The always growing demand for bio-based products cannot disregard the development of greener processes. Instead, the use of renewable raw materials and of environmentally benign techniques should proceed in a parallel way in order to reach a fully sustainable process.

The use of solid acid catalysts in esterification reactions has long been pursued as a significant step forward in this context. However, up to now effective solid catalysts for this reaction have rarely been reported due to easy deactivation of the surface as water forms.

The use of an amorphous solid catalyst, very resistant to water formed in the reaction and re-usable several times without the need of any treatment, not requiring neutralization and washing steps of the product, can be therefore a milestone in the road map to bio-based economy.

Acknowledgements

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